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Enhanced In Situ Bioremediation of BTEX-Contaminated Groundwater by Combined Injection of Nitrate and Sulfate

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Enhancement of in situ anaerobic biodegradation of BTEX compounds was demonstrated at a petroleum-contaminated aquifer in Seal Beach, CA. Specifically, combined injection of nitrate and sulfate into the contaminated aquifer was used to accelerate BTEX removal as compared to remediation by natural attenuation. An array of multi-level sampling wells was used to monitor the evolution of the in situ spatial distributions of the electron acceptors and the BTEX compounds. Nitrate was utilized preferentially over sulfate and was completely consumed within a horizontal distance of 4−6 m from the injection well; sulfate reduction occurred in the region outside the denitrifying zone. By combining injection of both nitrate and sulfate, the total electron acceptor capacity was enhanced without violating practical considerations that limit the amount of nitrate or sulfate that can be added individually. Degradation of total xylene appears linked to sulfate utilization, indicating another advantage of combined injection versus injection of nitrate alone. Benzene degradation also appears to have been stimulated by the nitrate and sulfate injection close to the injection well but only toward the end of the 15-month demonstration. The results are consistent with the hypothesis that benzene can be biodegraded anaerobically after other preferentially degraded hydrocarbons have been removed.

Introduction

Remediation by natural attenuation (RNA) is the preferred method (*1*) for addressing groundwater contamination by the aromatic fuel hydrocarbons benzene, toluene, ethylbenzene, and xylene (BTEX). However, there are certain conditions under which RNA is inadequate. For instance, at sites where the natural groundwater flow is very slow, intrinsic biodegradation processes can be limited by the rate at which the groundwater supplies electron acceptors and/or removes inhibitory byproducts (*2*). Furthermore, the effectiveness of removing benzene by RNA is still uncertain. Although anaerobic benzene biodegradation has been demonstrated (*3*−*14*), benzene has frequently been found recalcitrant under anaerobic conditions (*15*−*28*). This is of particular concern because benzene is the most toxic of the BTEX compounds. Because of these limitations to RNA, it is often necessary to enhance the natural attenuation processes by engineering the conditions at a contaminated site.

One way of doing this is by introducing additional electron acceptors into the aquifer, usually in aqueous solution. For instance, it has been suggested that introducing nitrate into contaminated groundwater as an electron acceptor can enhance in situ biodegradation and is sometimes capable of partially or completely removing BTEX (*22*, *29*−*33*). Also, it was recently demonstrated that the addition of sulfate to a petroleum-contaminated aquifer stimulated in situ anaerobic benzene degradation (*34*).

However, addition of a single electron acceptor might selectively stimulate the degradation of only certain BTEX compounds. For instance, in laboratory studies, sulfate addition has been observed to stimulate the degradation of benzene (*5*, *7*, *9*, *10*), toluene (*25*, *35*), and the three xylene isomers (*25*), but it has not yet been demonstrated that ethylbenzene can be degraded under strictly sulfate-reducing conditions. Furthermore, from an engineering perspective, there are practical limits to the electron acceptor concentrations that can be introduced in aqueous solution, as summarized in Table 1. Therefore, as compared to the injection of a single electron acceptor, the combined injection of more than one electron acceptor might be able to provide the dual advantages of (i) increasing the total electron acceptor capacity and (ii) increasing the potential for stimulating the degradation of all BTEX compounds.

In this paper, new results are reported from a recent field demonstration of enhanced in situ biodegradation of BTEX compounds at a petroleum-contaminated aquifer in Seal Beach, CA (*37*). The objective of this paper is to assess the efficacy of combined injection of nitrate and sulfate into the contaminated aquifer with regard to degradation of BTEX. The Seal Beach site has been the subject of previous laboratory (*9*, *25*, *27*, *38*) and field (*39*) studies, which had suggested that amendment of the groundwater with nitrate and/or sulfate could accelerate the biodegradation of BTEX. Addition of oxygen was intentionally excluded from the current study in order to better observe BTEX degradation under nitrate- and sulfate-reducing conditions, which are less understood than aerobic conditions. The hypotheses of the demonstration were that combined injection of nitrate and sulfate would (i) overcome the selectivity of each individual electron acceptor, (ii) provide a greater total electron acceptor capacity than injection of a single electron acceptor, and (iii) accelerate the BTEX degradation as compared to RNA.

Data from the demonstration are presented as time-varying two-dimensional contour plots of the concentrations of nitrate, sulfate, and BTEX. These graphs show the concentration variations with both length (distance from the injection well) and depth (depth below the water table). This approach allows the visualization of features such as the spatially variable electron acceptor utilization, the presence of a petroleum sheen floating on top of the water table, and the correlation of the BTEX concentrations with the electron acceptor concentrations. These are important features that cannot be observed by monitoring a single point in space or by monitoring vertically averaged concentrations.

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TABLE 1. Practical Limitations to Concentrations of Electron Acceptors That Can Be Added to Contaminated Groundwater in Aqueous Solution

electron acceptor	max concn (mg/L)	reason(s) for limitation	BTEX degrdn stoichiometry[a] (as toluene)	BTEX degraded[b] (mg/L)
O_2	9−10	aqueous solubility; aquifer clogging from biomass formation or from oxidation of Fe(II) to Fe(III)	$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$	2.9−3.2
NO_3^-	80−100	formation of N_2 gas bubbles in situ[c]; regulatory concern[d] over NO_3^-	$C_7H_8 + 7.2H^+ + 7.2NO_3^- \rightarrow 3.6N_2 + 7.6H_2O + 7CO_2$	16−21
SO_4^{2-}	100−250	formation of inhibitory sulfide[e]; secondary standard[f] for SO_4^{2-}	$C_7H_8 + 4.5SO_4^{2-} + 3H_2O \rightarrow 2.25HS^- + 2.25H_2S + 7HCO_3^- + 0.25H^+$	21−53
Fe^{3+}	0−1	Fe(III) salts have very low aqueous solubilities; aquifer clogging from precipitation of FeS	$C_7H_8 + 36Fe^{3+} + 21H_2O \rightarrow 36Fe^{2+} + 7HCO_3^- + 43H^+$	0−0.05

[a] Taken from ref *33*; assumes no cell growth. [b] Calculated as toluene degradation, using the electron acceptor concentration range and the stoichiometry shown in the table. Actual amount of BTEX degraded will be less if electron acceptors are consumed by other in situ processes or are not completely utilized. [c] Conversion of 90 mg/L NO_3^- to 20 mg/L N_2 exceeds the solubility limit for N_2 gas at ambient conditions. [d] Drinking water maximum contaminant level (MCL) for NO_3^- is 45 mg/L (10 mg/L as NO_3^--N). [e] Beller and Reinhard (*36*) reported that toluene degradation was inhibited by 1−3 mM sulfide in enrichment cultures. [f] Secondary standard for SO_4^{2-} in drinking water is 250 mg/L.

Demonstration Method

Site Description. The Naval Weapons Station (NWS), Seal Beach, is located in southern California. The soil and groundwater below a gasoline station on the premises of the NWS have been contaminated by fuel hydrocarbons that leaked from a steel underground storage tank (*40*). The gasoline leak was discovered in 1984. The following conditions made the NWS Seal Beach site particularly well-suited for this demonstration: (i) The groundwater in the contaminated zone had been anaerobic for at least a decade. Laboratory and field studies had demonstrated the presence of anaerobic bacteria capable of degrading fuel hydrocarbons. (ii) Previous studies at the site (*39*) indicated that the supply of electron acceptors and/or the removal of inhibitors are limiting, suggesting the need for enhancement of intrinsic biodegradation processes. (iii) The aquifer solids are sufficiently permeable. (iv) Laboratory and field data from previous studies (*9*, *25*, *27*, *38*, *39*) had suggested the probability of success of enhanced in situ bioremediation at the Seal Beach site.

The groundwater velocity in the region is low, approximately 0.7 cm/day (*39*). The groundwater flow rate and direction might fluctuate somewhat with the season and with the tides. The site hydrogeology and other details have been described by Schroeder (*40*).

Technology Description. The remediation technology included the installation of one extraction well and three injection wells into the contaminated aquifer, the relative locations of which are shown in Figure 1. Each injection well was located 10 m away from the extraction well. The injection wells and the extraction well were fully screened across the saturated zone of the aquifer. The rate of injection in each well was approximately 1.5 L/min; the rate of extraction was approximately 4.5 L/min. This configuration allowed the establishment of three different remediation zones, each with different geochemical conditions, as described elsewhere (*37*). The focus of this paper is zone 4, which received injection of both nitrate and sulfate in order to stimulate the biological oxidation of the BTEX compounds. In Figure 1, the approximate boundary of zone 4 is indicated by the shaded region. Some of the results from the other two zones have been discussed elsewhere (*37*).

Injection water was prepared from extracted water in the following manner. Extracted water was treated by activated carbon to remove BTEX and other fuel hydrocarbons, by ion exchange to remove nitrate and sulfate, and by helium stripping to remove dissolved oxygen. This was done in order to provide careful control over the injected electron acceptor concentrations for demonstration purposes. In a full-scale operation of this technology, if extracted water were re-

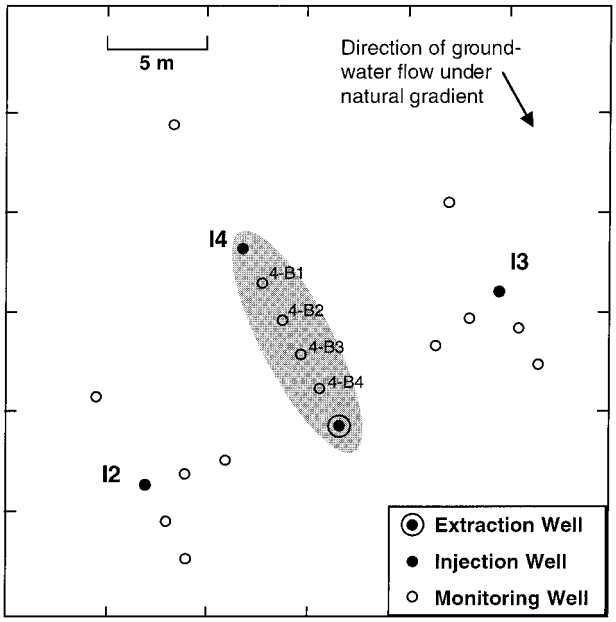

FIGURE 1. Relative locations of injection wells, extraction well, and monitoring wells at the Seal Beach demonstration site. The shaded area represents the approximate boundary of zone 4, which is the focus of this paper. Zone 4 was augmented with both nitrate and sulfate concurrently through injection well I4.

injected, the electron acceptors would not need to be removed prior to augmentation and re-injection. After being treated, the extracted water was augmented with electron acceptors in order to stimulate in situ biodegradation of the target contaminants and then was re-injected into the contaminated region of the aquifer, as shown in Figure 2.

Sampling and Analysis. As shown in Figures 1 and 2, there were four multi-level monitoring wells installed in zone 4 between the injection well and the extraction well. These four monitoring wells were evenly spaced 2 m apart from each other. We denote the location of the injection well as $x = 0$, and the locations of the monitoring wells as $x = 2$, 4, 6, and 8 m. The location of the extraction well is denoted $x = 10$ m. Each monitoring well had seven ports, evenly spaced about 35.5 cm apart. In each well, the top port was located very near the water table, and the bottom port was located about 2.1 m below the water table. The height of the water table is denoted $z = 0$ m, and the locations of the monitoring ports are $z = 0$, $z = -36$ cm, $z = -71$ cm, etc., down to $z = -213$ cm.

Sampling was performed automatically via an Automated Sampling and Analysis Platform (ASAP) from Analytic +

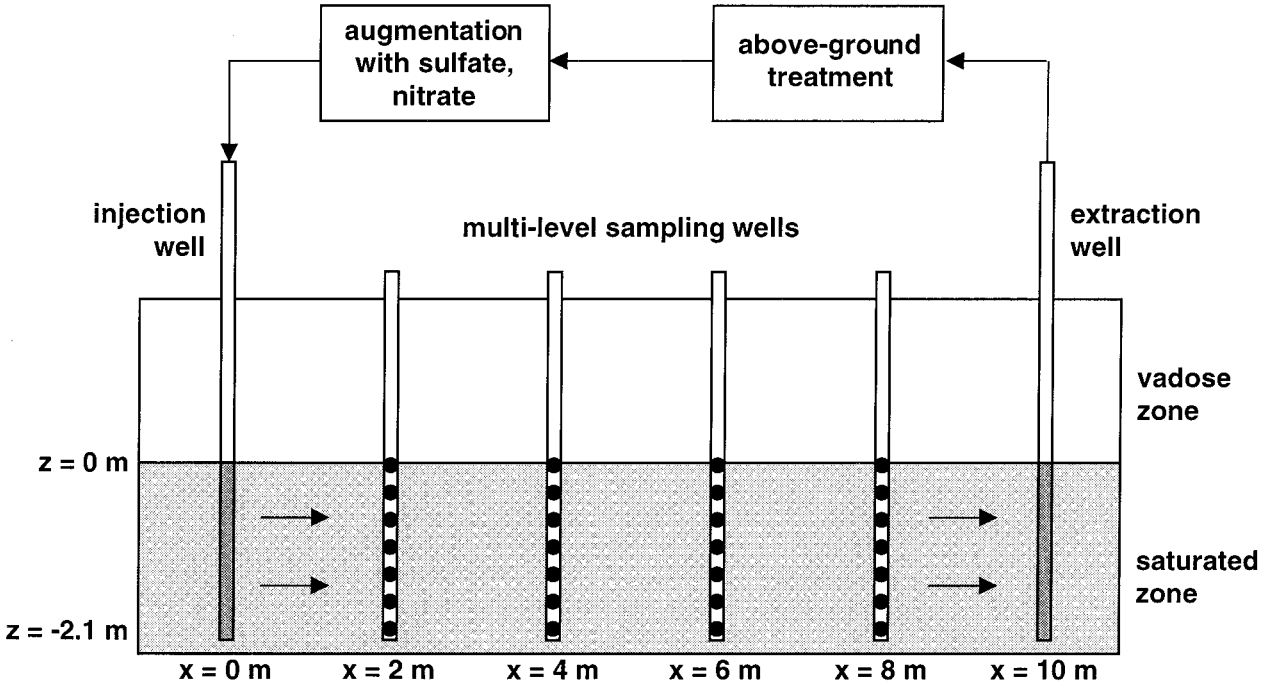

FIGURE 2. Schematic view of the treatment system. Extracted water was treated to remove the target contaminants and inhibitory compounds, then augmented with nitrate and sulfate, and then re-injected into the aquifer. Four multi-level monitoring wells were installed between the injection well and the extraction well, spaced evenly 2 m apart from each other. Each monitoring well had seven ports, evenly spaced about 35−36 cm apart, with the top port located at the water table. The height of the water table is denoted $z = 0$ m, and the locations of the monitoring ports are $z = 0$, −36, −71 cm, etc. down to $z = -213$ cm.

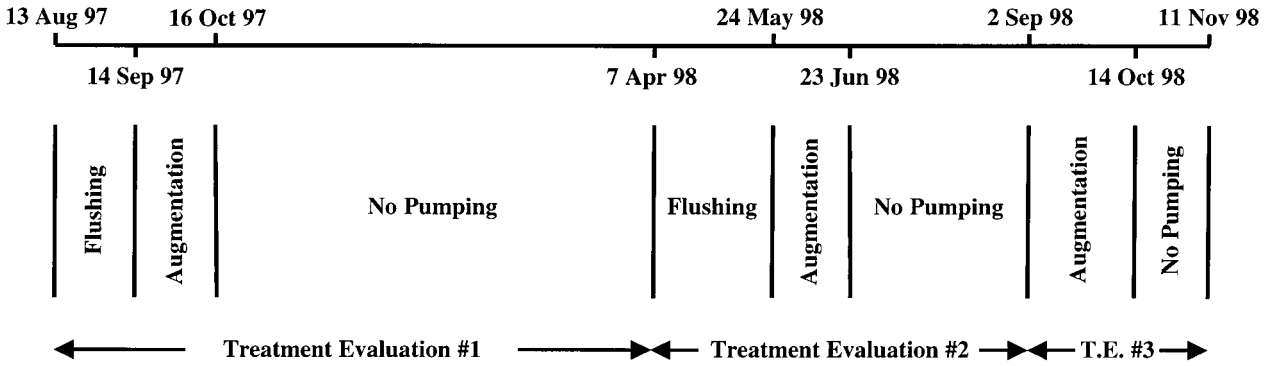

FIGURE 3. Timeline of the 15-month technology demonstration from August 1997 through November 1998. The treatment system can be operated in three modes: (i) injection/extraction with no augmentation of electron acceptors, i.e., flushing of the aquifer with unaugmented treated water; (ii) injection/extraction with augmentation of electron acceptors in the injection well; and (iii) no pumping, i.e., both injection and extraction wells are off. During the technology demonstration, one "treatment evaluation" consisted of operating in these three modes sequentially.

Remedial Technology (Milpitas, CA). The automated on-line sampling manifold consisted of 111 sample ports, of which 105 ports were connected directly to the multi-level sample bundles of the monitoring wells (see Figure 1). The remaining six ports were connected to the treatment system and to the three injection wells. The ASAP provided samples directly to the instrumentation with limited operator intervention and was operated continuously from August 1997 until November 1998. Connections between the monitoring wells and the ASAP were stainless steel tubing. After flushing the sample lines, the ASAP extracted a sample and prepared separate aliquots for analysis of: (1) concentrations of volatile organic compounds (including BTEX) via a modified purge-and-trap method with gas chromatography (GC), photoionization detection (PID), and flame ionization detection (FID); (2) concentrations of anions (including bromide, sulfate, and nitrate) via ion chromatography; and (3) pH, dissolved oxygen, and concentration of sulfide via specific probes. PID was used for the measurement of BTEX concentrations, and FID was used for the measurement of the concentrations of aliphatic hydrocarbons. Results from the ASAP analyses were automatically logged in a computer database.

System Operation. The system shown in Figures 1 and 2 can be operated in three modes: (1) injection/extraction with no augmentation of electron acceptors, i.e., flushing of the aquifer with unaugmented treated water; (2) injection/extraction with augmentation of electron acceptors in the injection well; and (3) no pumping, i.e., both injection and extraction wells are off. Hereafter, these three modes will be referred to as flushing, augmentation, and no-pumping, respectively. During the technology demonstration, one "treatment evaluation" consisted of operating in these three modes sequentially. The technology demonstration consisted of three treatment evaluations conducted over a 15-month period, as shown by the timeline in Figure 3.

During the flushing mode, the aquifer was flushed with water that had been treated to remove hydrocarbons, gases (including oxygen), and anions (including nitrate and sulfate)

TABLE 2. Concentrations of Electron Acceptors Injected into Zone 4 during the Augmentation Stage of the Three Treatment Evaluations

treatment evaluation	dates of augmentation	injected NO_3^- concn (mg/L)	injected SO_4^{2-} concn (mg/L)
1	Sep 14−Oct 16, 1997	15	15
2	May 24−Jun 23, 1998	45−55	70−80
3	Sep 2−Oct 14, 1998	85−125	70−100

but had not been augmented with electron acceptors. This served to remove inhibitory products (e.g., sulfide), to remove background concentrations of the electron acceptors, and to reduce the initial BTEX concentration. The flushing stage was implemented mainly to establish baseline conditions for evaluation purposes; at a full-scale implementation of this technology, the flushing stage might be omitted depending on whether inhibitory byproducts are present. For instance, as shown in Figure 3, the third treatment evaluation did not include a flushing stage.

During the augmentation mode, the aquifer was injected with treated water that had also been augmented with nitrate and sulfate. The augmentation stages lasted for about 4−5 weeks, thereby injecting enough water to develop a treatment zone of about 180 m^3 in size; because water was simultaneously being extracted, the actual size of the treatment zone was probably smaller. Table 2 shows the dates of the three augmentation stages and the concentrations of nitrate and sulfate injected in each of the augmentations. The concentrations of the injected electron acceptors were increased from one augmentation to the next in order to slowly build up the proper microbial population. During the no-pumping mode, both injection and extraction wells were shut off, and the aquifer was monitored to determine how the BTEX concentrations responded to the addition of the nitrate and sulfate.

During the no-pumping mode, the aquifer was under the influence of the natural groundwater flow, which is very slow; during the flushing and augmentation modes, the hydraulics are controlled by the pumping, with negligible influence from the natural gradient. A conservative tracer (bromide) study conducted during the flushing period of the first treatment evaluation showed that the travel time from the injection well to the extraction well is about 7−10 days when the pumps are in operation. The conservative tracer study also verified that the monitoring wells are hydraulically connected to the injection well.

Results and Discussion

Concentration Contour Plots. The results from this field demonstration are presented in the form of two-dimensional contour plots of BTEX concentrations and electron acceptor concentrations. Each plot exhibits the spatial distribution of the relevant compound in the aquifer at a particular date in time. Figure 4 shows an example of one such plot, for nitrate concentration on October 7, 1998. The contour plots are formed by using the data reported from the multi-level monitoring wells. There are four monitoring wells, each with seven ports, as shown in Figure 2. The top row of ports is located right at the water table, and water table fluctuations generally caused data from this row to be unavailable. Therefore, data from the lower six ports of each of the four monitoring wells were used, which yielded 24 concentration values for a selected date. Concentration values at locations other than these 24 monitoring ports were determined by piecewise bilinear interpolation of the monitoring well data. In addition, when the system was operated in augmentation mode, the injected concentration of the electron acceptors was known, which yielded data for the location $x = 0$, i.e., at the injection well.

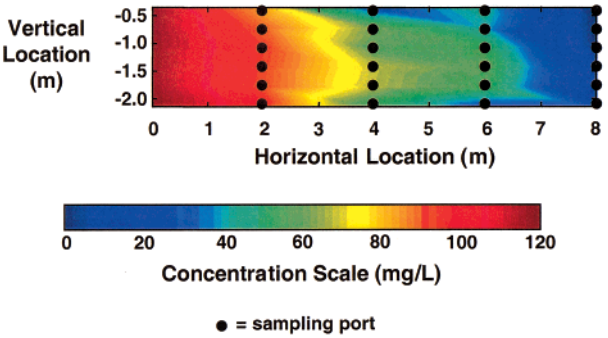

FIGURE 4. Example of a two-dimensional contour plot showing the spatial variability of nitrate concentration. The contour plot is formed by using the data reported from the 24 sampling ports shown in the figure. Concentration values at locations other than these 24 sampling ports were determined by piecewise bilinear interpolation of the monitoring well data. In addition, when the system was operated in augmentation mode, the injected concentration of the electron acceptors was known, which yielded data for the location $x = 0$, i.e., at the injection well. Because not all sampling ports were analyzed every day, a figure that is labeled "7 Oct 98" might actually include data from the time period October 5−9, 1998, i.e., samples were taken within 2 days of the nominal date shown.

Nitrate and Sulfate Utilization. Figure 5 shows the evolution of the nitrate and sulfate concentrations in zone 4 during the third of the three treatment evaluations. During this treatment evaluation, nitrate was injected at a concentration of 85−125 mg/L, and sulfate was injected at a concentration of 70−100 mg/L. During the first two treatment evaluations, nitrate and sulfate were injected at lower concentrations, as shown in Table 2. At the lower concentrations, sulfate and especially nitrate were consumed within a very short distance of the injection well, and the results from those treatment evaluations are not presented.

The augmentation stage of the third treatment evaluation ran from September 2, 1998 to October 14, 1998. Figure 5 indicates that, during this time period, nitrate was rapidly utilized, presumably for the oxidation of petroleum hydrocarbons. A conservative tracer broke through to $x = 10$ m within a time period of 7−10 days (data not shown); however, even after 6 weeks of injection, nitrate only reached a distance of about $x = 6$ m and was mostly consumed within about 4 m of the injection well. Once the injection and extraction wells were shut off on October 14, 1998, and the no-pumping stage began, nitrate was utilized rapidly, disappearing significantly within 1 week and almost completely within 4 weeks.

In contrast to nitrate, sulfate broke through at its injected concentration to a distance of approximately $x = 6$ m during the augmentation stage. However, Figure 5 shows that sulfate was utilized in the region $x = 6$−8 m during this time. This is consistent with previous observations that sulfate is biologically utilized only where nitrate is not present, i.e., nitrate is used preferentially over sulfate (e.g., refs *27* and *41*). Once the augmentation stage ended, sulfate was not significantly consumed during the first week of the no-pumping period, perhaps because there was still some nitrate present during that time. However, by the end of 4 weeks of the no-pumping stage, sulfate had begun to disappear, indicating biological utilization. Once nitrate had been depleted, sulfate was utilized in the region 2−6 m from the injection well, where denitrification had occurred. This indicates that sulfate-reducing organisms in that region were not damaged by the establishment of the denitrifying community.

During the third treatment evaluation, approximately 9 kg of nitrate was injected, all of which was consumed;

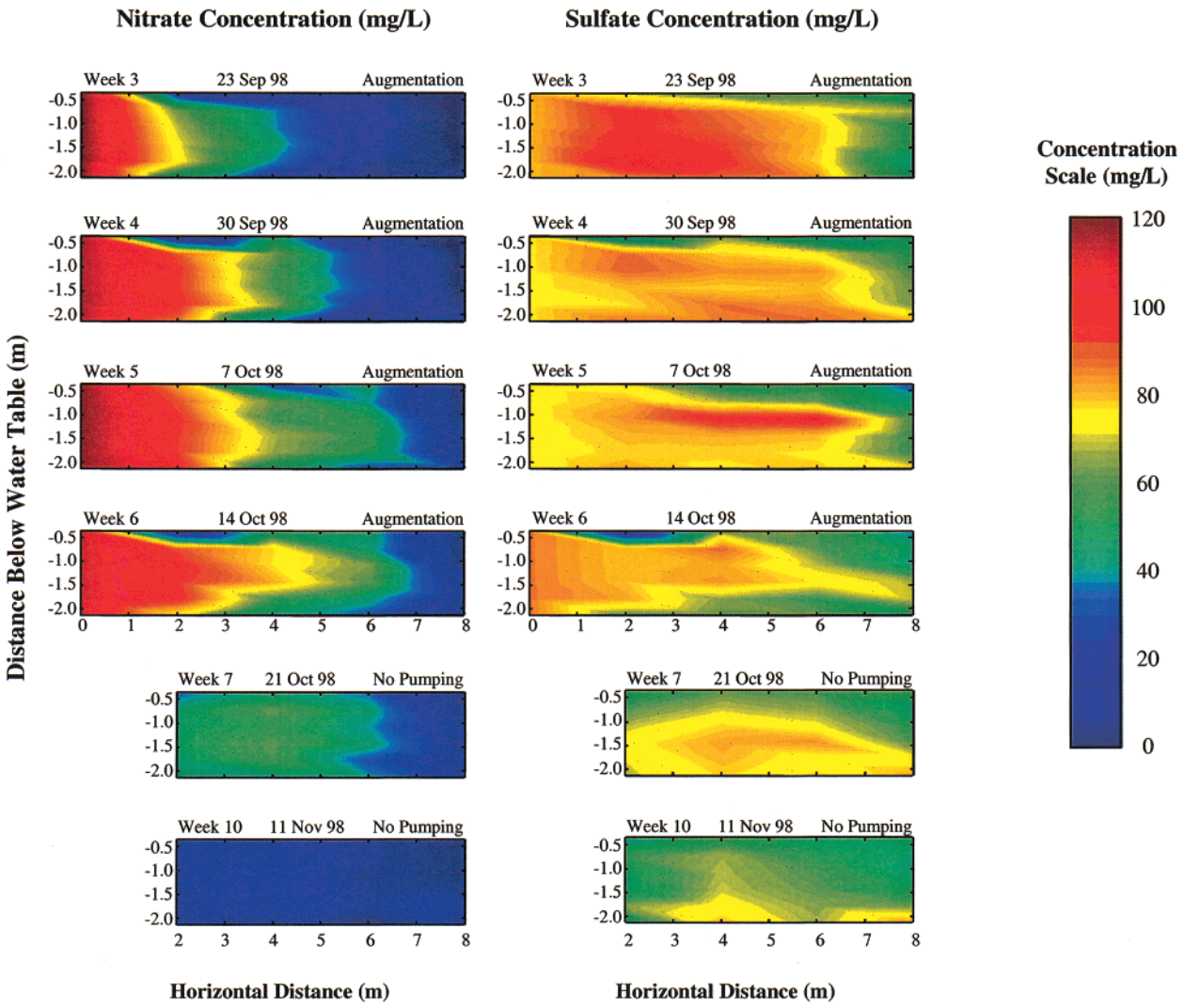

FIGURE 5. Evolution of nitrate and sulfate concentrations in zone 4 during the third of the three treatment evaluations. During this treatment evaluation, nitrate was injected at a concentration of 85−125 mg/L, and sulfate was injected at a concentration of 70−100 mg/L. The augmentation stage ran from September 2, 1998, until October 14, 1998, at which point the injection and extraction wells were shut off, beginning the no-pumping stage. During the augmentation stage, the travel time from the injection well to the extraction well is about 7−10 days; during the no-pumping stage, there is essentially no groundwater flow.

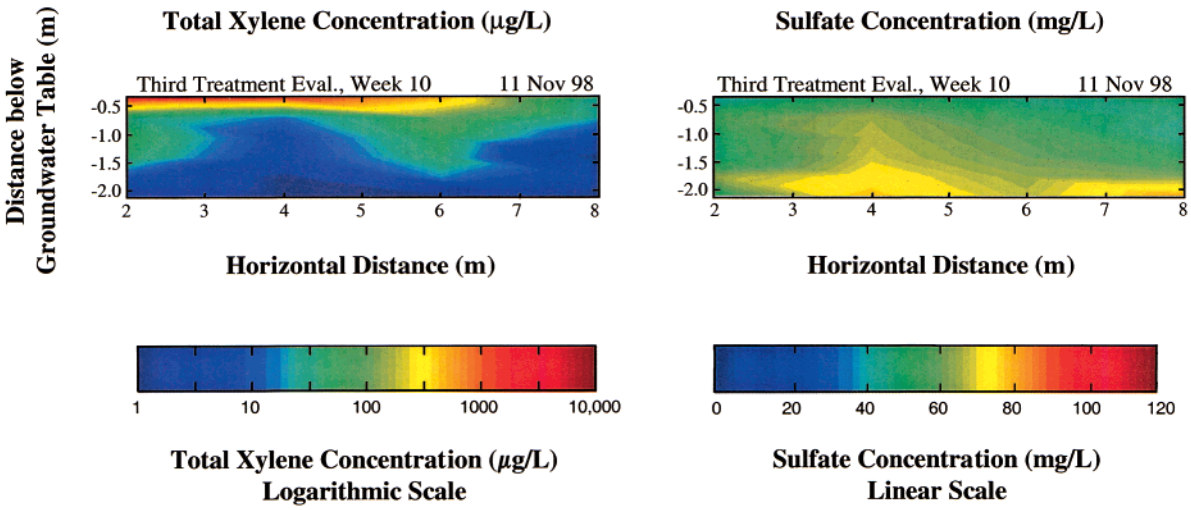

FIGURE 6. Concentration profiles for total xylenes and for sulfate at the end of the 15-month demonstration on November 11, 1998. The concentration scale for total xylenes is logarithmic, while that for sulfate is linear. These figures show the concentration profiles during a no-pumping stage, 4 weeks after sulfate augmentation ended.

approximately 8 kg of sulfate was injected, most of which was consumed. Using the stoichiometries shown in Table 1, these amounts of electron acceptors would have oxidized approximately 3.5 kg of fuel hydrocarbons, which is higher than expected based on the initial aqueous BTEX concentrations. This indicates that the electron acceptors were also consumed by fuel hydrocarbons other than BTEX and/or that a continuing source of BTEX was present in the aquifer, e.g., by dissolution of a nonaqueous-phase liquid (NAPL) residual.

These results demonstrate that the combined injection of both nitrate and sulfate can offer an advantage over injection of just one or the other by increasing the total electron acceptor capacity. Injection of sulfate alone would not be as effective because nitrate is utilized preferentially and is able to more rapidly oxidize the petroleum hydrocarbons. Injection of nitrate alone would establish a biologically active zone that extends approximately 4−6 m from the injection well. By injecting both nitrate and sulfate, a sulfate-reducing zone is established beyond the denitrifying zone, beginning at approximately $x = 6$ m and extending to at least $x = 8$ m. The establishment of this sulfate-reducing zone is a significant benefit as compared to injection of nitrate alone. Furthermore, as discussed below, it appears that sulfate utilization is closely linked to the degradation of the xylene isomers.

(Total) Xylene Degradation. Figure 6 shows the concentration profile for total xylenes (sum of ortho, meta, and para isomers) at the end of the 15-month demonstration on November 11, 1998. Note that the concentration scale for total xylenes is logarithmic. The concentration profile of sulfate is also shown. Figure 6 shows a very strong negative correlation between the total xylene concentration and the sulfate concentration: where the total xylene concentration was high, there was very little sulfate present, and where the sulfate concentration was high, there was very little total xylene present. This is a clear indication that xylene degradation and sulfate utilization are linked. Therefore, injection of sulfate is expected to accelerate the biodegradation of total xylenes as compared to injection of nitrate alone. This is an example of how combined injection of nitrate and sulfate removes the selective limitations that might be encountered by injection of just one or the other.

The other important feature to notice in Figure 6 is that the concentration of xylene remained high in the upper portion of the aquifer, near the water table. During the demonstration, the Seal Beach site still had a petroleum sheen floating on top of the water table in a nonaqueous phase. This NAPL represented a continuing source of petroleum contamination. Vertical diffusion from the water table into the lower portions of the aquifer is relatively slow, so that the BTEX concentrations in the lower portions of the aquifer could be remediated to relatively low levels, as seen in Figure 6. Nevertheless, the continuing presence of xylenes near the water table underscores the importance of source removal in a full-scale remediation.

Benzene Removal. At most petroleum-contaminated groundwater sites, benzene is the compound of greatest concern, both because it has a low drinking water MCL (5 μg/L) and because it is fairly recalcitrant to anaerobic biodegradation. Figure 7 shows six graphs that illustrate the behavior of benzene over the course of this demonstration. The six graphs are alternately from augmentation stages and no-pumping stages, as indicated on the figure.

Figure 7 shows that benzene concentrations underwent a cycle of attenuation and rebound during the demonstration. Benzene concentrations decreased during the augmentation stages and then rebounded during the no-pumping stages. This behavior is commonly seen when pump-and-treat remediation is applied to contaminated groundwater sites

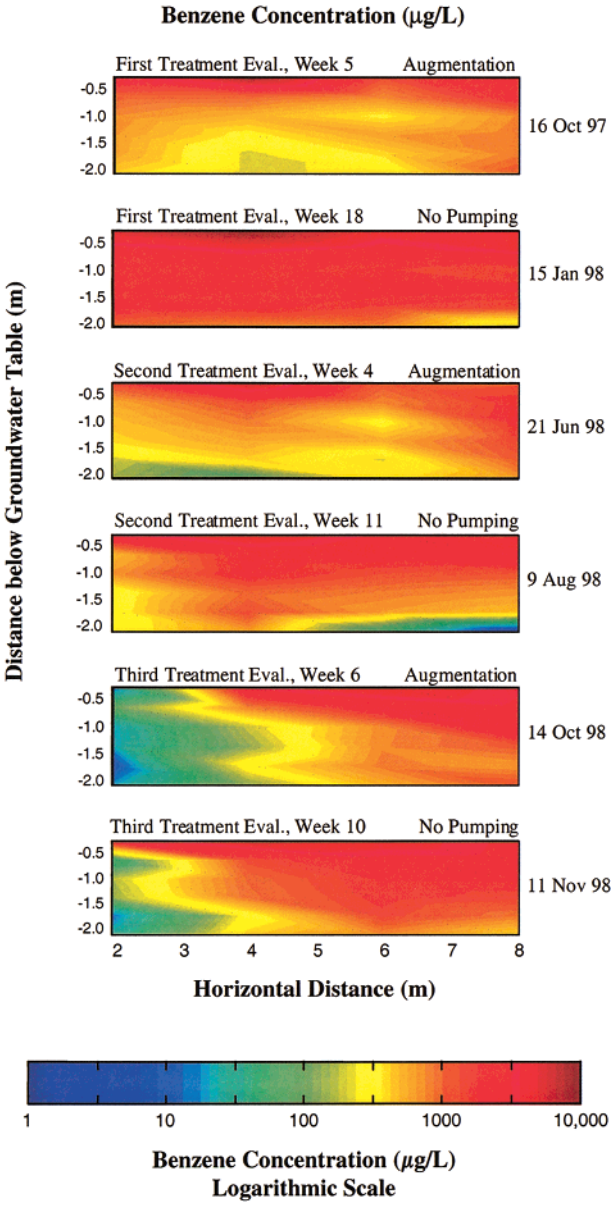

FIGURE 7. Behavior of benzene over the course of the three treatment evaluations of this demonstration. The profiles are alternately from augmentation stages and no-pumping stages, as indicated on the figure. The top two graphs are from the first treatment evaluation, the middle two are from the second treatment evaluation, and the bottom two are from the last treatment evaluation.

(*42*−*44*). At the Seal Beach site, it is believed that the benzene rebound was caused by dissolution of entrapped NAPL below the water table. Other phenomena could also be responsible for this rebound, including (i) vertical diffusion of benzene from the NAPL-contaminated water table to the lower portions of the aquifer, (ii) slow flow of benzene-laden groundwater into the demonstration zone, and/or (iii) slow desorption of benzene from aquifer solids into the groundwater. However, diffusion is a very slow process, as is groundwater flow under natural-gradient conditions, so neither of these mechanisms appears responsible for the rebound. Benzene does not sorb very strongly to the aquifer materials at Seal Beach (unpublished data), so desorption is not likely responsible for the rebound either. The most likely candidate is that there was NAPL present below the water table and that this NAPL slowly dissolved into the aqueous phase during the demonstration.

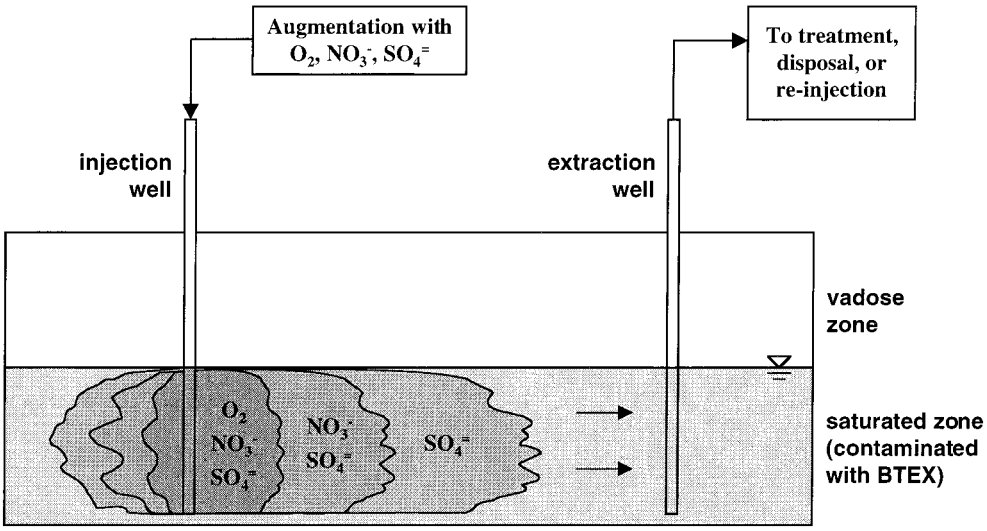

FIGURE 8. Representation of the geochemical zones that are expected be established upon the combined injection of oxygen, nitrate, and sulfate.

More importantly, Figure 7 suggests that benzene was biodegraded during the third treatment evaluation. If benzene removal were due to flushing out in the extraction well, then we would expect to see relatively uniform removal throughout the aquifer, as observed during the first two treatment evaluations. The preferential removal of benzene near the injection well during the augmentation stage of the third treatment evaluation suggests biodegradation as a removal mechanism rather than flushing. This idea is further supported by the consideration that the region near the injection well is the region that was exposed to the highest concentrations of electron acceptors (both nitrate and sulfate) throughout the 15-month demonstration. The observed pattern of increasing benzene concentration downgradient probably indicates that a source of benzene (e.g., from NAPL dissolution) is present a few meters from the injection well.

It has been hypothesized previously (*9*, *45*) that anaerobic benzene degradation is possible but is impeded by the presence of other, preferentially degradable hydrocarbons. Such a hypothesis is consistent with the data shown in Figure 7. It appears that, during the first two treatment evaluations, the electron acceptors were utilized for the degradation of fuel hydrocarbons other than benzene and that benzene was removed by flushing only, but that by the third treatment evaluation, the area near the injection well was sufficiently clear of other hydrocarbons that benzene could be biodegraded.

Such a conclusion bears important implications. For one thing, it implies that RNA would be a very slow method of remediating a site like Seal Beach. Prolonged exposure to the electron acceptors was required before benzene biodegradation commenced, and the supply of electron acceptors is very slow under natural conditions. The injection of nitrate and sulfate was able to stimulate benzene biodegradation after approximately 1 yr of operation by removing the other hydrocarbons that limit benzene degradation. It is important to note that, at the end of the 15-month demonstration, only a very small portion of the aquifer had been remediated to a benzene concentration below the MCL of 5 μg/L. However, the last two graphs of Figure 7 suggest that, if the system had been operated longer, biodegradation would have removed benzene from the aquifer, beginning in the vicinity of the injection well and moving outward toward the extraction well.

Extension to Full-Scale Implementation. One goal of this project was to demonstrate a technology that could be used at BTEX-contaminated groundwater sites, particularly those where natural conditions would not make RNA a viable option. To this end, it is important to consider how the technology described in this paper would be altered for commercial application. For instance, as discussed previously, the following changes might be made. (i) Electron acceptors would not need to be removed in the above-ground treatment system. (ii) The flushing mode of the system operation might not be needed, depending on whether inhibitory byproducts were known to be present. (iii) Removal of any NAPL source from above the water table would be important to prevent continuous re-contamination of the aquifer regions near the water table (as seen in Figures 6 and 7).

Furthermore, one way in which the technology could be improved at a full-scale implementation would be to include dissolved oxygen along with nitrate and sulfate in the injected water. This project intentionally omitted oxygen in order to investigate nitrate- and sulfate-reducing conditions. However, at a full-scale implementation, oxygen should be included. We have demonstrated that the combined injection of nitrate and sulfate yields advantages over the injection of just one or the other; including oxygen would provide further benefits. Oxygen is consumed preferentially over nitrate or sulfate and would be consumed within a very short distance of the injection well. This is particularly true because the solubility of O_2 in water is relatively low at ambient conditions (about 9−10 mg/L) and because oxygen is highly reactive in reduced groundwater. Also, the electron-donating capacity of oxygen is low as compared to those of nitrate and sulfate, as shown in Table 1. Nevertheless, petroleum hydrocarbons (including benzene) are biodegraded rapidly under aerobic conditions (*46*), so injection of oxygen would only be expected to improve the overall system performance. Figure 8 shows a schematic of what the geochemical zones might look like with the combined injection of oxygen, nitrate, and sulfate.

Of course, site-specific characteristics must be accounted for in applying this technology. For instance, if the BTEX contamination can be easily flushed out of the aquifer, then conventional pump-and-treat might be sufficient. However, at Seal Beach, the injection of nitrate and sulfate offered a strong advantage over pump-and-treat by significantly degrading fuel hydrocarbons in situ as well as removing them in the above-ground treatment system.

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